Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Theoretical study on the effect of different substituents on the electronic structures and photophysical properties of phosphorescent Ir(III) complexes

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Table S1. Calculated phosphorescent emission wavelength (nm)/energies (eV) of the complexes **1** and **4** in CH_2Cl_2 media with the TDDFT method at the B3LYP, M062X and PBE0 level, respectively, together with the experimental values

	λ_{cal}/E(eV) (PBE0)	λ_{cal}/E(eV) (B3LYP)	λ_{cal}/E(eV) (M062X)	λ_{cal}/E(eV) (M052X)	Exp.[15]
1	562	563	476	499	520
4	548	540	467	493	499

Table S2. Molecular orbital composition (%) of **1** in the ground state.

MO	Energy(eV)	Composition (100%)				Assign
		Ir	ppy1	ppy2	PPh_2^SiO	
L + 5	-0.29	4	4	4	88	π*(PPh_2^SiO)
L + 4	-0.49	1	71	13	15	π*(ppy + PPh_2^SiO)
L + 3	-0.58	1	0	16	83	π*(ppy + PPh_2^SiO)
L + 2	-0.66	2	16	66	16	π*(ppy + PPh_2^SiO)
L + 1	-1.05	4	83	10	4	π*(ppy)
LUMO	-1.16	4	10	85	2	π*(ppy)
HOMO	-5.08	40	30	15	14	d(Ir) + π(ppy + PPh_2^SiO)
H-1	-5.66	53	5	17	24	d(Ir) + π(ppy + PPh_2^SiO)
H-2	-5.88	1	27	31	41	π(ppy + PPh_2^SiO)
H-3	-6.00	18	20	38	24	d(Ir) + π(ppy + PPh_2^SiO)
H-4	-6.20	22	47	17	14	d(Ir) + π(ppy + PPh_2^SiO)
H-5	-6.27	1	5	74	21	π(ppy + PPh_2^SiO)

Table S3. Molecular orbital composition (%) of **2** in the ground state.

MO	Energy(eV)	Composition (100%)				Assign
		Ir	ppy1	ppy2	$P(CH_3)_2$^SiO	
L + 5	-0.04	1	0	4	95	π*($P(CH_3)_2$^SiO)
L + 4	-0.32	2	1	3	94	π*($P(CH_3)_2$^SiO)
L + 3	-0.55	1	45	51	3	π*(ppy)
L + 2	-0.68	2	53	43	2	π*(ppy)
L + 1	-1.12	4	26	69	1	π*(ppy)
LUMO	-1.17	3	70	26	1	π*(ppy)
HOMO	-5.07	39	26	20	14	d(Ir) + π(ppy + $P(CH_3)_2$^SiO)
H-1	-5.65	50	5	19	25	d(Ir) + π(ppy + $P(CH_3)_2$^SiO)
H-2	-5.92	0	32	30	38	π(ppy + $P(CH_3)_2$^SiO)
H-3	-6.10	19	15	43	24	d(Ir) + π(ppy + $P(CH_3)_2$^SiO)
H-4	-6.23	13	18	59	11	d(Ir) + π(ppy + $P(CH_3)_2$^SiO)
H-5	-6.29	22	32	29	18	d(Ir) + π(ppy + $P(CH_3)_2$^SiO)

Table S4. Molecular orbital composition (%) of **3** in the ground state.

MO	Energy(eV)	Composition (100%)				Assign
		Ir	ppy1	ppy2	PH_2^SiO	
L + 5	-0.12	1	0	5	94	π*(PH_2^SiO)
L + 4	-0.49	2	11	3	83	π*(ppy + PH_2^SiO)
L + 3	-0.64	2	48	43	7	π*(ppy)
L + 2	-0.78	2	39	51	8	π*(ppy)
L + 1	-1.20	4	76	19	2	π*(ppy)
LUMO	-1.26	4	19	76	2	π*(ppy)
HOMO	-5.25	38	31	21	11	d(Ir) + π(ppy + PH_2^SiO)
H-1	-5.91	46	9	31	15	d(Ir) + π(ppy + PH_2^SiO)
H-2	-6.11	13	38	35	14	d(Ir) + π(ppy + PH_2^SiO)
H-3	-6.31	13	33	18	36	d(Ir) + π(ppy + PH_2^SiO)
H-4	-6.37	12	28	50	11	d(Ir) + π(ppy + PH_2^SiO)
H-5	-6.44	5	19	54	22	π(ppy + PH_2^SiO)

Table S5. Molecular orbital composition (%) of **4** in the ground state.

MO	Energy(eV)	Composition (100%)				Assign
		Ir	dfppy1	dfppy2	PPh_2^SiO	
L + 5	-0.48	4	5	6	85	π*(PPh_2^SiO)
L + 4	-0.60	1	71	10	18	π*(dfppy + PPh_2^SiO)
L + 3	-0.72	1	2	46	51	π*(dfppy + PPh_2^SiO)
L + 2	-0.79	2	10	37	51	π*(dfppy + PPh_2^SiO)
L + 1	-1.22	4	86	6	4	π*(dfppy)
LUMO	-1.33	4	6	88	2	π*(dfppy)
HOMO	-5.44	40	28	14	19	d(Ir) + π(dfppy + PPh_2^SiO)
H-1	-5.92	49	4	22	25	d(Ir) + π(dfppy + PPh_2^SiO)
H-2	-6.18	1	25	25	49	π(dfppy + PPh_2^SiO)
H-3	-6.24	14	55	19	13	d(Ir) + π(dfppy + PPh_2^SiO)
H-4	-6.33	8	20	61	10	π(dfppy + PPh_2^SiO)
H-5	-6.48	4	18	47	31	π(dfppy + PPh_2^SiO)

Table S6 Optimized S_0 structure for $(ppy)_2Ir(PPh_2\text{^}SiO)$ (**1**)

Ir	0.81490400	-0.16027700	-0.10224000	C	-2.05514500	4.15977200	-0.42383700
P	-1.58964700	0.10309000	0.26709000	H	-1.65096900	4.92341500	-1.08679600
Si	-0.25443200	2.52643500	-1.88431000	C	-3.00941400	4.53554300	0.51573800
N	1.46538200	1.43554700	1.04511700	H	-3.34084900	5.56929800	0.57794200
N	0.48210400	-1.84283300	-1.20590900	C	-3.52953200	3.57605100	1.37646900
O	0.24186000	0.99301700	-1.83560700	H	-4.27217000	3.84613400	2.12295900
C	2.75154300	-0.08338900	-0.67173800	C	-3.09694100	2.25723400	1.28056800
C	3.41551700	-0.90966500	-1.58592200	H	-3.51187000	1.52176600	1.96164400
H	2.89087200	-1.74113800	-2.04780200	C	-2.62429600	-0.62150300	-1.06902800
C	4.74544200	-0.68753100	-1.93003500	C	-2.75726400	-2.01478600	-1.13631000
C	5.45974600	0.37249000	-1.36837000	H	-2.26664700	-2.64301800	-0.39687900
H	6.49655000	0.54590700	-1.64288100	C	-3.52180000	-2.60505600	-2.13687400
C	4.83214100	1.20234900	-0.45362000	H	-3.61539000	-3.68722900	-2.17288600
C	3.49418400	0.97431700	-0.10269300	C	-4.15907100	-1.81336800	-3.09021800
C	2.77282500	1.78375400	0.86643600	H	-4.75559600	-2.27458600	-3.87299000
C	3.32750500	2.83317600	1.60822700	C	-4.03207300	-0.42898600	-3.03084700
H	4.36667200	3.09870900	1.45173600	H	-4.53108000	0.19764900	-3.76545800
C	2.56442800	3.51809900	2.53675100	C	-3.27274900	0.16478000	-2.02430000
H	2.99684100	4.33278000	3.11069900	H	-3.19552900	1.24626900	-1.97747700
C	1.23817400	3.13625100	2.72406600	C	-2.38370600	-0.64258400	1.75210900
H	0.59260100	3.63122400	3.44117800	C	-1.60536900	-0.86377300	2.89196600
C	0.73747800	2.09631400	1.96093500	H	-0.54253800	-0.64736800	2.86630500
H	-0.28971500	1.77738700	2.07408000	C	-2.17218800	-1.40079200	4.04606200
C	1.30653400	-1.54641300	1.25843100	H	-1.54733400	-1.57768100	4.91730200
C	1.82678200	-1.37776400	2.55238500	C	-3.52439300	-1.72581600	4.07387100
H	2.00152000	-0.37315900	2.93238700	H	-3.96633600	-2.15025600	4.97160100
C	2.12394000	-2.46302700	3.37025500	C	-4.30984600	-1.51478400	2.94146400
C	1.92256500	-3.77087700	2.92200300	H	-5.36614400	-1.77072700	2.95454200
H	2.15118800	-4.61639200	3.56468500	C	-3.74509000	-0.97900400	1.78875600
C	1.44351800	-3.97752300	1.63801200	H	-4.36436200	-0.82129500	0.91017500
C	1.14940700	-2.88571600	0.81030700	H	5.23323600	-1.34602400	-2.64565300
C	0.70960300	-3.02518500	-0.57180000	H	5.38920400	2.02865600	-0.01854300
C	0.55144200	-4.22147300	-1.27962200	H	1.30524900	-4.99541900	1.28004500
H	0.73003300	-5.16646700	-0.77841900	H	2.52177100	-2.29174100	4.36859200
C	0.19430400	-4.19308700	-2.61875400	C	-1.04158000	2.91158900	-3.56128600
H	0.08244800	-5.12204700	-3.17148800	H	-1.50601600	3.90494800	-3.58881600

C	-0.00995400	-2.96549700	-3.24595300	H	-0.27308600	2.88326200	-4.34371400
H	-0.28710900	-2.89924700	-4.29239900	H	-1.80476600	2.17093700	-3.82464300
C	0.13788700	-1.80694100	-2.50104700	C	1.08812400	3.83211200	-1.60492500
H	-0.00275200	-0.80175100	-2.89164600	H	1.43232100	3.86609500	-0.56599900
C	-2.13917300	1.87554900	0.32939600	H	1.95463700	3.59616300	-2.23459500
C	-1.58820000	2.84159300	-0.54572600	H	0.74515600	4.83812000	-1.87771800

Table S7 Optimized S_0 structure for $(ppy)_2Ir(P(CH_3)_2$^SiO) (**2**)

Ir	0.45976100	0.03194400	-0.04156400	H	4.41864200	-3.51553000	-2.55621400
P	-0.90893400	-1.85574300	0.50888200	C	2.59275700	-2.40201300	-2.86276200
Si	-2.37331500	0.15020700	-1.91031300	H	2.47280600	-2.66804900	-3.90754700
N	-0.62509500	1.52004900	0.89739400	C	1.66207800	-1.57914600	-2.25086800
N	1.77480800	-1.22674700	-0.96149600	H	0.78522700	-1.16469600	-2.74443800
O	-0.77344300	-0.05512000	-1.82133600	C	-2.72218500	-1.54654700	0.52245400
C	1.43763700	1.67226200	-0.72271900	C	-3.30318100	-0.72421700	-0.47101400
C	2.55086000	1.73102200	-1.57025300	C	-4.69079200	-0.52714900	-0.40286900
H	3.02938300	0.81393800	-1.90331000	H	-5.17210100	0.09945200	-1.15211600
C	3.06601900	2.94569300	-2.01222500	C	-5.48171300	-1.09400800	0.59237600
C	2.48392100	4.15196800	-1.61762800	H	-6.55342700	-0.91120000	0.60979300
H	2.88481600	5.09888600	-1.96847800	C	-4.89027900	-1.89026300	1.56675400
C	1.38879600	4.12918600	-0.76933100	H	-5.49044900	-2.33779300	2.35493600
C	0.87511700	2.90429200	-0.32066900	C	-3.51738500	-2.11441000	1.52733900
C	-0.24953300	2.79705600	0.59473900	H	-3.06975800	-2.73938000	2.29473000
C	-0.91676500	3.88061000	1.17861200	H	3.93033400	2.95610500	-2.67309200
H	-0.60994400	4.88843600	0.92363300	H	0.93723100	5.06966500	-0.46254900
C	-1.94725600	3.67140800	2.07699200	H	4.61241900	-2.13343000	1.85466300
H	-2.46325600	4.51423900	2.52808600	H	2.67955600	0.44185800	4.67741300
C	-2.30216900	2.36230200	2.39434200	C	-3.04257100	-0.63135000	-3.49874300
H	-3.09837400	2.13603500	3.09498900	H	-4.13177000	-0.53389400	-3.58359500
C	-1.61706900	1.32767900	1.78273500	H	-2.59474000	-0.14635400	-4.37470200
H	-1.87472700	0.29812800	1.99049100	H	-2.79924000	-1.69928400	-3.54978200
C	1.76200100	-0.22901500	1.45295100	C	-2.94257700	1.95464500	-1.87821400
C	1.74909900	0.31976600	2.74524000	H	-2.75518900	2.42735500	-0.90791500
H	0.96179900	1.01724300	3.02171100	H	-2.38500800	2.52086400	-2.63413200
C	2.72096000	-0.00371300	3.68549600	H	-4.01071700	2.06260000	-2.10415900
C	3.75347200	-0.89284300	3.37209600	C	-0.76554400	-3.24479000	-0.68540600
H	4.50904800	-1.14324700	4.11141200	H	0.25122500	-3.64972400	-0.66831700
C	3.80617800	-1.44659500	2.10308500	H	-1.47804300	-4.03734400	-0.43557000
C	2.83028900	-1.11855100	1.15120200	H	-0.97734500	-2.86773400	-1.68923700
C	2.82884500	-1.64229100	-0.20791000	C	-0.53686100	-2.69930600	2.09764300
C	3.78828300	-2.48431200	-0.78232000	H	-0.75071800	-2.03681700	2.94207400
H	4.62871400	-2.82244100	-0.18603600	H	-1.07503900	-3.64430500	2.22376400
C	3.67071500	-2.86661800	-2.10873400	H	0.54011000	-2.89667700	2.11015100

Table S8 Optimized S_0 structure for $(ppy)_2Ir(PH_2\text{^}SiO)$ (**3**)

Ir	0.29513700	-0.09302800	-0.07897200	C	3.47277500	-1.23609000	2.48126500
P	-1.15658700	-1.89896100	0.45620500	C	2.56209900	-1.05735300	1.43108300
Si	-2.34459800	-0.00603200	-2.11820700	C	2.65303700	-1.77004300	0.16401100
N	-0.86561900	1.49124600	0.56348500	C	3.64231200	-2.68589200	-0.21212100
N	1.65402100	-1.47739300	-0.71176600	H	4.44245700	-2.92243200	0.48045700
O	-0.78790100	-0.38959800	-1.95457100	C	3.60025000	-3.27668400	-1.46446100
C	1.34384000	1.44928600	-0.85656800	H	4.37041700	-3.98470100	-1.75797000
C	2.53252500	1.40092100	-1.59279200	C	2.56555700	-2.95159700	-2.34187000
H	3.03011700	0.44946600	-1.76017400	H	2.50058500	-3.38890800	-3.33235700
C	3.09759500	2.55289800	-2.13194300	C	1.60653700	-2.04292800	-1.92723900
C	2.48931100	3.79634800	-1.95096600	H	0.76344600	-1.71962600	-2.53397300
H	2.93033400	4.69293000	-2.37746800	C	-2.95992200	-1.67546700	0.22793900
C	1.31542100	3.87725300	-1.21907700	C	-3.44798400	-0.88082500	-0.82864100
C	0.75018700	2.71768900	-0.67134800	C	-4.83709100	-0.72835500	-0.93091300
C	-0.46215200	2.72082400	0.13337400	H	-5.24536700	-0.12613200	-1.74197500
C	-1.18574000	3.86116200	0.49989700	C	-5.71463800	-1.32013700	-0.02723100
H	-0.85848700	4.83162900	0.14501700	H	-6.78720200	-1.17928700	-0.13551900
C	-2.30000300	3.75418000	1.31213700	C	-5.21335900	-2.09203700	1.01744100
H	-2.86056700	4.64063600	1.59495500	H	-5.88733000	-2.55754300	1.73173200
C	-2.68271000	2.49353800	1.76476000	C	-3.83950000	-2.26883700	1.14296700
H	-3.54340600	2.35130400	2.40887500	H	-3.45070700	-2.87518500	1.95828700
C	-1.93964300	1.39776200	1.36496900	H	4.02139600	2.48352500	-2.70228200
H	-2.21011900	0.39923500	1.68296900	H	0.84313700	4.84673100	-1.07995600
C	1.46934000	-0.15515500	1.53974600	H	4.30151400	-1.93365200	2.38237800
C	1.35537700	0.55635400	2.74285900	H	2.14470100	0.94700800	4.70213200
H	0.54254300	1.26705700	2.87052400	H	-1.15890600	-2.57645700	1.70078100
C	2.26231100	0.37785700	3.78230800	H	-0.87091400	-3.01559000	-0.36438500
C	3.32512200	-0.52094400	3.65874400	H	-2.89399000	-0.43523200	-3.44631900
H	4.03008400	-0.65630700	4.47411400	H	-2.68689900	1.45101500	-1.98265000

Table S9 Optimized S_0 structure for $(dfppy)_2Ir(PPh_2\text{^}SiO)$ (**4**)

Ir	0.55733400	0.04771300	-0.15206500	C	-2.73608000	4.07245800	0.10784900
P	-1.86469800	0.02532100	0.19761300	H	-2.39566700	4.96778800	-0.41023000
Si	-0.72984300	2.87966900	-1.50111400	C	-3.75414400	4.19714700	1.04740100
N	1.06554500	1.49535800	1.23705300	H	-4.19645200	5.16937800	1.25067500
N	0.37282700	-1.46251000	-1.50948000	C	-4.19540800	3.06725600	1.72621500
O	-0.07952200	1.41278000	-1.67997500	H	-4.98616600	3.14072700	2.46837600
C	2.48578300	0.35816100	-0.65760200	C	-3.61969000	1.83078600	1.45273500
C	3.19285200	-0.27707300	-1.68000700	H	-3.97339600	0.95940400	1.99370600
H	2.74809700	-1.05541500	-2.28979600	C	-2.80091600	-0.59925500	-1.25480600
C	4.50034100	0.09300900	-1.94796200	C	-2.81012800	-1.97629700	-1.51477100
C	5.16224000	1.08441700	-1.23665400	H	-2.28785000	-2.65871000	-0.84893500
H	6.18394300	1.36499300	-1.46115900	C	-3.49364800	-2.48380600	-2.61424800
C	4.45810700	1.70262600	-0.22268200	H	-3.49272600	-3.55467700	-2.79907200
C	3.13692700	1.36624600	0.09753700	C	-4.17053300	-1.62292600	-3.47608100
C	2.34701100	1.96421000	1.16117400	H	-4.70375900	-2.01921000	-4.33617900
C	2.79731700	2.92234400	2.08023200	C	-4.16483400	-0.25414900	-3.22623300
H	3.81236200	3.28339100	2.00472100	H	-4.69568800	0.42451300	-3.88864400
C	1.95380100	3.39042000	3.07247600	C	-3.48759700	0.25576600	-2.12016400
H	2.30772700	4.13183300	3.78312500	H	-3.50470000	1.32317800	-1.92534300
C	0.65602200	2.89392100	3.14489000	C	-2.57389000	-1.00085300	1.55044000
H	-0.04718400	3.22389000	3.90159500	C	-1.80411400	-1.22641300	2.69575600
C	0.26080300	1.95386200	2.21027000	H	-0.78920300	-0.84646800	2.74315800
H	-0.74370400	1.55366400	2.22672800	C	-2.31335500	-1.96523700	3.76117900
C	1.13366800	-1.48856500	0.99371300	H	-1.69535600	-2.13880100	4.63795900
C	1.61628300	-1.45326500	2.30869700	C	-3.59972200	-2.49128400	3.69371100
H	1.71221000	-0.51747200	2.85126900	H	-3.99581600	-3.07373800	4.52132200
C	1.98118600	-2.62506300	2.94913300	C	-4.37634500	-2.27465800	2.55690800
C	1.90046300	-3.87240700	2.34301200	H	-5.38137200	-2.68392400	2.49649300
H	2.18510000	-4.78023700	2.86033300	C	-3.86930300	-1.53497400	1.49317000
C	1.45303100	-3.90211600	1.03656700	H	-4.48304100	-1.37200500	0.61199600
C	1.07882200	-2.75206300	0.33322300	F	5.16441400	-0.52379800	-2.93399800
C	0.67826900	-2.71431400	-1.06679400	F	5.10699700	2.66629400	0.46040200
C	0.62759100	-3.78634000	-1.96748100	F	2.42598800	-2.56737500	4.21246300
H	0.86479700	-4.78211400	-1.62100200	F	1.38903400	-5.11087900	0.44536100
C	0.30093300	-3.55693000	-3.29563700	C	-1.50621600	3.44847800	-3.12911100
H	0.27617900	-4.38801300	-3.99528400	H	-2.19248800	2.69446200	-3.53047300
C	0.01597200	-2.26267100	-3.72255100	H	-2.05847600	4.39044300	-3.02470700

H	-0.24021300	-2.04333700	-4.75328200	H	-0.71930700	3.60677800	-3.87684600
C	0.05498800	-1.23770100	-2.79214800	C	0.46419800	4.24439500	-0.95926400
H	-0.15514600	-0.19483300	-3.01805900	H	0.79196900	4.13090900	0.07940700
C	-2.59680300	1.70314600	0.50139200	H	1.35726500	4.21830400	-1.59544800
C	-2.12648300	2.84380900	-0.19127300	H	0.01690400	5.24124900	-1.06056800